Influence of side groups on 90° superexchange: A modification of the Goodenough-Kanamori-Anderson rules

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A mechanism is suggested which can modify in certain cases the Goodenough-Kanamori-Anderson rules determining the character of superexchange in magnetic insulators; namely, side groups coupled to ligands, which are often present but are usually ignored, may contribute significantly, and may in certain cases even lead to a change in sign of the superexchange interaction. Thus this factor can make the 90° superexchange of half-filled shells antiferromagnetic, in contrast to the usual case. Qualitative arguments and numerical estimates show that this mechanism may be important in the inorganic spin-Peierls compound $CuGeO_3$. [S0163-1829(96)02829-9]

As is well known, the exchange interaction in magnetic insulators is predominantly caused by the so-called superexchange — which is due to the overlap of the localized orbitals of the magnetic electrons with those of intermediate ligands. There exist different processes contributing to the superexchange interaction which appear under various names in the various calculational schemes: delocalization superexchange, potential exchange, indirect exchange, kinetic exchange, correlation exchange, ring exchange, etc. (see, e.g.,[1-4] and below). Nevertheless, usually most of these partial processes give results which follow the so-called Goodenough-Kanamori-Anderson (GKA) rules. According to these rules for instance, a 180° superexchange (the magnetic ion–ligand–magnetic ion angle is 180°) of two magnetic ions with partially filled d shells is strongly antiferromagnetic, whereas a 90° superexchange is ferromagnetic and much weaker.

Recently, several materials were studied in which these rules seem to be violated, or at least their validity is questionable. One of such systems which now attracts considerable attention is $CuGeO_3$—the first inorganic compound showing a spin-Peierls transition.[5] The main feature of the crystal structure[6-9] of $CuGeO_3$ is shown in Fig. 1. It consists of CuO_2 ribbons with a nearly square planar coordination of the Cu^{2+} ions by O^{2-}. The Cu ions are coupled by an O pair bridge. The Cu–O–Cu angle is $\phi \approx 98°$, which is rather close to 90^0. However, the superexchange interaction between nearest neighbor Cu atoms is antiferromagnetic:[5,10] $J \approx -3$ to -6.5 meV (we define J by the exchange Hamiltonian: $H = -2J\mathbf{S}_1\mathbf{S}_2$). The question arises why this Cu-Cu superexchange interaction is antiferromagnetic, while the well-known GKA rules predict a ferromagnetic superexchange interaction for the 90° cation-ligand-cation configuration.

In this paper we discuss some of the basic structural and electronic features which may lead to such a violation of the GKA rules. In order to keep the presentation simple and clear we use a simple perturbation theory scheme[1,3] and consider the smallest cluster possible in order to emphasize the physics involved. The detailed discussion of the superexchange interaction in $CuGeO_3$, taking into account all de-

tails of the structure, will be given in a separate paper. The localized orbitals we consider are shown in Fig. 2. On the (magnetic) cations $M_{1,2}$, we consider only a half-filled $d_{x'^2-y'^2}$ orbital and on the ligands $L_{1,2}$, we take the $p_{x'}$ and $p_{y'}$ orbitals. The σ-type covalent mixing parameter between the ligand p and cation d orbital is defined by $\lambda = \langle d|H_{\mathrm{eff}}|p\rangle/\Delta$, where $\Delta = \epsilon_d - \epsilon_p$, and $\langle d|H_{\mathrm{eff}}|p\rangle$ is the transfer integral, which is often called t_{pd}.

Let us first discuss briefly the basis of the GKA rules for the sign of the 90° configuration. In the standard theory underlying these rules one considers a number of processes contributing to superexchange in which each mechanism has a definite sign: positive for a ferromagnetic interaction, negative for an antiferromagnetic interaction.

Two ferromagnetic contributions are illustrated in Figs. 3(a) and 3(b). The first one is caused by the real ferromagnetic exchange between one magnetic cation and a ligand p orbital polarized by another cation. It gives

$$J_a = 4\lambda^2 J_{pd}, \tag{1}$$

where $J_{pd} \sim 0.01 - 0.05$ eV. The second ferromagnetic contribution is due to a Hund's rule exchange interaction J_H on a
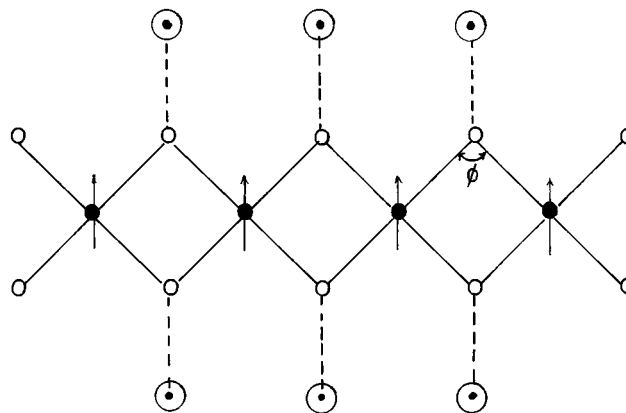

FIG. 1. One of the basic structural units of the $CuGeO_3$ structure: the one-dimensional $[CuO_2]$ ribbon. ●: Cu^{2+}; ○: O^{2-}; ☉: Ge^{4+}.
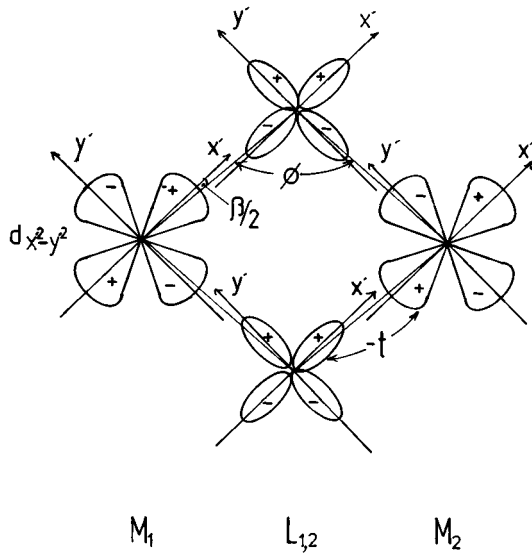
FIG. 2. M_2L_2 cluster for 90° superexchange. The angle β is the deviation from 90°. The M_1-L_1-M_2 angle is $\phi = \pi/2 + \beta$. The $d_{x'^2-y'^2}$ orbitals on M_1 and M_2 and the $p_{x'}$ and $p_{y'}$ orbitals on the ligands L_1 and L_2 are shown. The transfer matrix element between ligand p and magnetic d orbital is t.

ligand when two ligand electrons from different p orbitals are virtually transferred to the cations, Fig. 3(b). It gives

$$J_b = 2\lambda^4 J_H(L), \qquad (2)$$

where $J_H(L) \sim 0.5$–1.5 eV. The magnitude of these two mechanisms does not strongly depend on deviations from the ideal 90° configuration which we will assume in the following discussion.

Two principal antiferromagnetic contributions are the so-called delocalization, or kinetic superexchange, Fig. 3(c), and the correlation superexchange, Fig. 3(d). Both of these contributions require the transfer of electrons between cations and the *same* ligand orbital, and for 90° geometry these terms do not contribute because such a transfer is forbidden by symmetry. Thus we see that in standard cases 90° superexchange of half-filled shells is indeed ferromagnetic, which explains one of the GKA rules.

Let us now turn our attention to the factors which can make these symmetry-forbidden transfers possible. The obvious one is a deviation from 90°, to be discussed later. Another, less obvious source comes from the presence of side groups interacting with the intermediate ligands.

The main idea may be explained as follows. Whereas for pure 90° geometry the $p_{x'}$ and $p_{y'}$ orbitals are strictly orthogonal, which prevents the antiferromagnetic superexchange, the presence of a side group (Ge) attached to a ligand violates this orthogonality. In other words, a $p_{x'}$ hole existing in an intermediate state can make "a detour" to a side group and then return onto a $p_{y'}$ orbital of oxygen, thus giving finally an antiferromagnetic contribution.

Let us consider this effect in some detail. It is convenient to rotate the coordinate system for the $p_{x'}$ and $p_{y'}$ orbitals on the ligand over 45° as shown in Fig. 4. When the p_x and p_y orbitals are equivalent it is clear that cation-ligand-cation transfer paths tend to cancel: they interfere destructively.
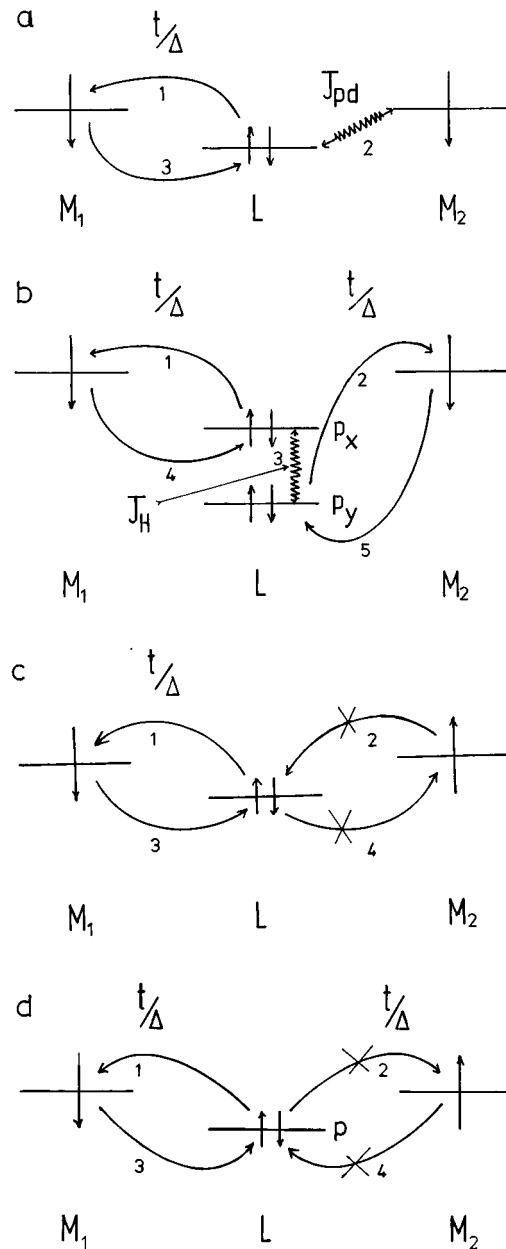

FIG. 3. Graphical representation of the perturbation expansion of the virtual electron transfer processes considered in the main text, which give the main contribution to 90° cation (M_1)-ligand ($L_{1,2}$)-cation (M_2) superexchange. The numbers indicate the order of the subsequent transfers (t/Δ) and Hund's rule interactions (J_H) in the perturbation expansion. The contributions t/Δ to the perturbation expansion are indicated. The sign of each virtual transfer depends on the phase of the wave functions. ——×——: symmetry-forbidden virtual transfer. Wavy line: exchange interaction.

However, if the p_x and p_y are inequivalent, such a cancellation does not happen. The presence of side groups really makes these two p orbitals inequivalent.

Side groups have two effects on the ligand p orbitals. First, due to the lattice potential, the p_y orbital has an energy different from that of the p_x orbital: a high positive charge on the side group, as, for instance, for Ge^{4+} in $CuGeO_3$, will make the electronic p_y orbital more stable than the p_x orbital
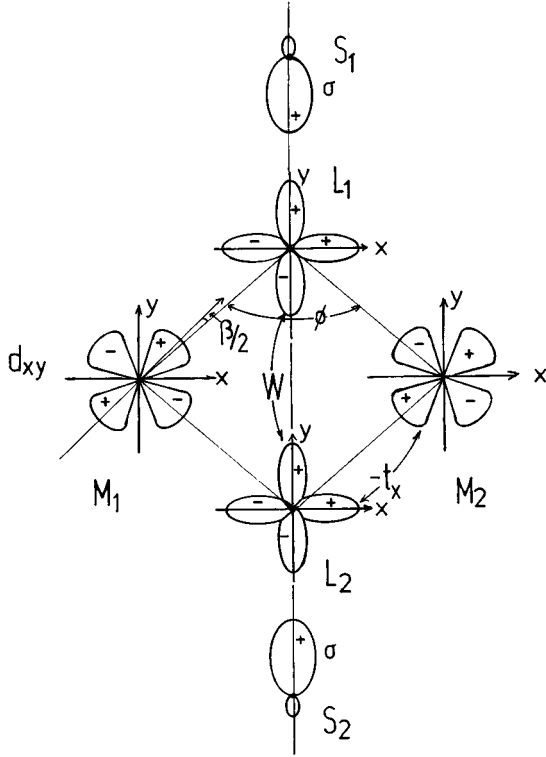
FIG. 4. The M_2L_2-S_2 cluster. The axes x' and y' are rotated over 45° to x and y, with respect to those used in Fig. 2. The σ bonding orbitals on the side groups S_1 and S_2 are indicated. The angle β is the deviation from ideal 90° geometry. t_x is the transfer integral between d_{xy} and p_x, and W is the transfer integral between the p_y orbitals on the two ligands L_1 and L_2.

by an amount δ. Also, a large hybridization of the ligand p_y orbital with a σ bonding side group orbital (for Ge an sp^3 orbital) can give the p_y orbital an appreciable shift with respect to the p_x orbital. Another factor, which also leads to inequivalence of transfer paths, is the p-p hybridization in the O pair bridge $W=\langle p_y(L_1)|H|p_y(L_2)\rangle$.

We find now the expression for the kinetic exchange—the process shown in Fig. 3(c)—taking into account (1) the deviation from ideal geometry, (2) the pp hybridization W, and (3) the energy shift of the p_y orbital with respect to the p_x orbital due to side group effects. This expression has the form

$$J_{\text{kin}}=-\frac{8}{U_d}(\lambda_x^4\Delta_x^2+\lambda_y^4\Delta_y^2-2\lambda_y^2\lambda_x^2\Delta_x\Delta_y)$$

$$=-\frac{8}{U_d}(\lambda_x^2\Delta_x-\lambda_y^2\Delta_y)^2, \tag{3}$$

where the excitation energies include the pp covalency and the side group effect; $\Delta_x=\Delta$ as defined above, and $\Delta_y=\Delta+W+\delta$. The covalency parameters include the geometrical factor: $\lambda_x=\lambda\sin(\phi)\sin(\phi/2)$ and $\lambda_y=\lambda\,\eta\sin(\phi)\cos(\phi/2)$, where η takes into account that part of the p orbital is hybridized into an antibonding ligand–side group orbital. The first term in Eq. (3) is due to transfer via p_x orbitals only, the next via p_y orbitals, and the last is a

cross term where part of the transfer is via p_x and part via p_y orbitals. Note that J_{kin} vanishes in the case of equivalent p_x and p_y orbitals.

Next we consider the correlation and ring exchange, where by ring exchange we mean the process of virtual transitions involving the excitation M_1-L_1-M_2-L_2-M_1. For these contributions we get

$$J_{\text{cor}}=-8\lambda_x^4\Delta_x^2\left(\frac{1}{2\Delta_x}+\frac{1}{\Delta_{xx}}\right)-8\lambda_y^4\Delta_y^2\left(\frac{1}{2\Delta_y}+\frac{1}{\Delta_{yy}}\right)$$

$$+4\lambda_x^2\lambda_y^2(\Delta_x+\Delta_y)^2\left(\frac{1}{\Delta_{xy}}+\frac{1}{\Delta_x+\Delta_y}\right), \tag{4}$$

where the excitation energies are $\Delta_{\alpha\beta}=\Delta_\alpha+\Delta_\beta+U_{\alpha\beta}^p$ (α and β refer to the ligand p orbitals); $U_{\alpha\beta}^p$ is the Coulomb interaction in the *ligand p* orbitals. The terms with $\Delta_{\alpha\beta}$ are contributions involving excitations from one ligand, while the terms with Δ_α are due to excitations from p orbitals on different ligands.

It is now instructive to expand these superexchange contributions Eq. (4) in $U_{\alpha\beta}^p/(\Delta_\alpha+\Delta_\beta)$. One then obtains the above discussed ferromagnetic contribution [Eq. (2)] with $2J_H=U_{xx}^p-U_{xy}^p$. The remaining contribution is

$$J'_{\text{cor}}=-8(\lambda_x^2\Delta_x-\lambda_y^2\Delta_y)(\lambda_x^2-\lambda_y^2). \tag{5}$$

Again, this contribution vanishes in the case of equivalent ligand orbitals.

We consider now separately the factors contributing to an antiferromagnetic interaction. For the contribution due to the deviation of the Cu-O-Cu angle from 90°, denoted by β, we find the geometrical contribution

$$J_{\text{geo}}=-8\lambda^4\Delta\left(1+\frac{\Delta}{U_d}\right)\beta^2, \tag{6}$$

where the parameters λ and Δ refer to the situation with equivalent p orbitals.

Next we consider contributions due to the presence of side groups. For weak ligand p_y–side group σ hybridization we may take $\eta^2\approx\delta/\Delta_\sigma$, where Δ_σ is the energy difference between the ligand p orbital and the side group σ orbital. We find the following result:

$$J_{\text{side group}}=-2\lambda^4\frac{\Delta^2}{U_d}\left(\frac{\delta}{\Delta_\sigma}+\frac{\delta}{\Delta}\right)^2$$

$$-2\lambda^4\Delta\left(\frac{\delta}{\Delta_\sigma}+\frac{\delta}{\Delta}\right)\left(\frac{\delta}{\Delta_\sigma}+2\frac{\delta}{\Delta}\right). \tag{7}$$

The first term is the kinetic and the second the correlation contribution.

The effect of the O pair bridge hybridization of the p_y orbitals gives

$$J_{\text{hybr}}=-2\lambda^4\left(2+\frac{\Delta}{U_d}\right)\frac{W^2}{\Delta}. \tag{8}$$

In addition to these three terms (6)–(8) there are cross terms between these three effects. These cross terms also add up to an antiferromagnetic contribution.

Let us give a quantitative estimate of these superexchange contributions for the $CuGeO_3$ compound. We estimate the parameters by assuming that the geometrical contribution has to reproduce the exchange constant in the high-T_c cuprate compounds for 180° geometry. We take (see Refs. 11 and 12) $t_{pd}=1.0$ eV, $\Delta=4.0$ eV, $U_d=7$ eV, $J_H(O)=0.4$ eV, $\beta=8°$, $W=0.7$ eV. For the dp exchange we take $J_{pd}=0.025$ eV. For the shift of the p_y orbital with respect to the p_x orbital we take $\delta \approx 0.4$ eV. For the energy difference between the side group orbital σ and the anion p orbital we take $\Delta_\sigma \approx 4$ eV.

We obtain for the covalency parameter $\lambda=t_{pd}/\Delta=0.25$. Then we find $J \approx -50$ meV for the cuprates. For $CuGeO_3$ we find for the ferromagnetic contributions $J_a=6.3$ meV and $J_b=3.1$ meV. So the total ferromagnetic contribution to superexchange is 9.4 meV. For the quadratic antiferromagnetic contributions we find $J_{geo}=-3.8$ meV, $J_{side group}=-2.6$ meV, and $J_{hybr}=-2.5$ meV. To this we have to add the cross terms between these three (geometrical, side group, and pp hybridization) effects, and we find a total contribution of the quadratic and cross terms to the superexchange of -15.1 meV. The sum of all ferromagnetic and antiferromagnetic contributions is $J=-5.8$ meV and is antiferromagnetic. It compares well with the nearest neighbor superexchange derived from various experiments for $CuGeO_3$. Furthermore, we find that when the shift δ of the p_y level due to the side group vanishes we will still find a small ferromagnetic interaction of 0.3 meV for the total superexchange.

From this simple example it is clear that the deviation from 90° is not sufficient to make the superexchange interaction antiferromagnetic. Such a small effect on the total superexchange interaction due to the deviation from ideal 90° geometry is also found in an *ab initio* calculation on a Cu_2O_6 cluster.[13] Only an appreciable energy shift of one of the intermediate ligand p orbitals with respect to the other p orbital involved in the transfer paths, which is caused by the influence of a side group (Ge), can change the sign of the superexchange interaction from ferromagnetic to antiferromagnetic.

We conclude that side groups, which are often present but are usually ignored, can significantly modify the 90° superexchange and, in certain cases, can cause an apparent violation of the GKA rules (cf. also Refs. 14 and 15). In particular, such groups attached to bridging anions can make the 90° superexchange antiferromagnetic. We have shown that this factor plays an important role in the mechanism of the superexchange interaction in the spin-Peierls system $CuGeO_3$. The great sensitivity of the total exchange to the side groups may probably explain a change in properties of $CuGeO_3$ when Ge is substituted[16,17] by Si (this question is now under investigation).

Superexchange is also very sensitive to the Ge-O distance and to the angle between the Ge-O bond and the Cu-O-Cu plane. A change in these parameters may significantly modify the resulting Cu-Cu exchange. The driving force for the spin-Peierls transition may thus well be the sensitivity of the superexchange interaction to the side group. The modulation of the superexchange interaction is then partially caused by a modulation in the interatomic Ge-O distance and/or (Cu-O-Cu)-(Ge-O) angle which accompanies the observed distortion.[6] (For a different interpretation, see Ref. 18.)

There exist other systems where we expect a significant influence of side groups on superexchange, e.g., organometallic and bioinorganic compounds as discussed in Ref. 15. This side group mechanism may also be of relevance in other inorganic materials, e.g., the layered magnetic semiconductors of the kind $ACrS_2$ and $ACrSe_2$, where A is a monovalent ion Li, Na, K, Ag, or Cu.[19]

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